REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE (DD-MM-YYYY) 15-10-2003	2. REPORT TYPE Final Report	3. DATES COVERED (From – To) 3 September 2002 - 03-Sep-03

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
New Organometallic Polymers And Hybrid Organo-Inorganic Composites Exhibiting Fast Kerr-Type And Photorefractive Non-Linearities.	FA8655-02-M4074
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Professor William Douglas	5d. TASK NUMBER
	5e. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Universite de Montpellier II Laboratorie Chimie Moleculaire et Organisation du Solide Place E. Bataillon Montpellier 34095 France	8. PERFORMING ORGANIZATION REPORT NUMBER N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0014	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) SPC 02-4074

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

20040809 018

14. ABSTRACT

This report results from a contract tasking Universite de Montpellier II as follows: The contractor will investigate the nonlinear optical properties of organic and organo-metallic polymers and hybrid organic-inorganc composites. These materials exhibit strong nonlinear properties with fast (femtosecond) response times. These materials are potentially useful for optical switching of telecommunications devices, phase conjugation, optical limiters, and optical multiplexing. Advances in these subjects can significantly improve performance of Air Force optical and telecommunications systems.

15. SUBJECT TERMS
EOARD, Polymer Chemistry, Organic nonlinear optical materials, Organic-inorganic materials, Nonlinear Optics

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18, NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON CHARLES H. WARD, Lt Col, USAF
a. REPORT UNCLAS	b. ABSTRACT UNCLAS	c. THIS PAGE UNCLAS		19	19b. TELEPHONE NUMBER (Include area code) +44 (0)20 7514 3154

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39-18

Contract SPC 024074

Contract Order Number FA8655-02-M-4074

EOARD Liaison Officer : Dr Alex Glass (Charles H. Ward, Lt Col, USAF as from 21.8.3)

Principal Investigator : Dr William Douglas

ITEM 004 - FOURTH (FINAL) REPORT covering the period 3rd June 2003 to 2nd September 2003

Investigation of the Cubic Non-Linearity of New Organometallic Cyano-containing Polymers by Z-scan and Two Beam Coupling with Spectral Resolving

Summary

The third order nonlinear-optical properties of a variety of new organochromium CN-containing polymers have been investigated by z-scan and two beam coupling with spectral resolving in the pico- and femtosecond ranges.

Z-scan picosecond measurements on films of different compositions of the materials showed the third order nonlinear optical susceptibility to lie in the range 5.5×10^{-12} - 1.7×10^{-10} esu. The carbon-nitrogen conjugated ladder chains length was established to be a factor of major importance. The domination of the very short polyacrylonitrile chains giving a short π-conjugated system as well as the presence of the crosslinking centers interrupting π-conjugation give rise to a decrease in the nonlinear optical properties. The results are also consistent with the arene ligand covalent bonding with PAN having a beneficial influence on the third order nonlinear optical susceptibility.

Large nonlinear coefficients of third order nonlinear optical susceptibility were also found with femtosecond time of initialization. Investigations using a femtosecond laser and a new sensitive method of spectrally resolved two-beam coupling have confirmed the studies in the picosecond range, the main results being the existence of a large electronic optical nonlinearity in the samples studied.

The possibility of fast optical switching by using a nonlinear Fabry-Pérot interferometer containing a nonlinear polymer layer has been shown. Sharp dependencies of the nonlinear resonator propagation coefficient on the peak intensity (or pulse energy at fixed duration) are obtained for certain parameters of this device, such as reflection coefficients of the front and back mirrors, layer width and nonlinear refractive index of the polymer.

AQ F04-09-1014

TABLE OF CONTENTS

1.   State-of-the-art of the project implementation

During the final quarter of the present project we have pursued our research by studying the nonlinear optical properties of the new organochromium polymeric compositions.

Previously, we have reported the extraordinarily high non-resonant cubic optical nonlinearity exhibited by this type of materials. The goal of this study is to investigate the dominant factors determining the level of fast optical nonlinearity of the materials based on the bis(arene)chromium complex incorporated into CN-containing organic polymers - polyacrylonitrile (PAN) and polyethylcyanoacrylate (PECNA) - in order to use the information obtained for composition optimization.

To this end during the fourth quarter of this project we have firstly undertaken picosecond Z-scan measurements of the cubic nonlinear optical properties of the various compositions in films. The third order nonlinear optical susceptibilities are found to lie in the range 5.5×10^{-12} - 1.7×10^{-10} esu for the different compositions. The length of the carbon-nitrogen conjugated ladder chain was established to be a factor of major importance. The domination of very short polyacrylonitrile chains giving a short π-conjugated system as well as the presence of crosslinking centers interrupting π-conjugation decrease the nonlinear optical properties. The results are also consistent with the arene ligand covalent bonding with PAN having a beneficial influence on the third order nonlinear optical susceptibility.

Secondly, for the investigations in the femtosecond range of laser pulse duration, we have used a new experimental method of two beam coupling with spectral resolving for the testing beam. This method allows the avoidance of including mechanisms of optical nonlinearity with relatively long period of initialization (longer than hundreds of femtoseconds) into the final

figure of nonlinearity. It does not require a sophisticated experimental setup and it is more sensitive than similar methods (for example, based on autocorrelation function analysis). In this new method there is no requirement for large intensities of testing beams in order to obtain large nonlinear phase shifts in nonlinear samples. The nonlinear phase shift 0.01 rad can be easily detected with a peak intensity of some GW/cm^2 of femtosecond pulse. The simplicity of setup alignment is the most significant advantage. The negative side of this method is its high sensitivity to external noise, instabilities of laser beam and spectrum of laser radiation and defects of sample surface.

The third direction of our scientific activity during the last quarter of this project was the theoretical investigation of the possibility of fast optical switching. The main idea of fast optical switching in a nonlinear Fabry-Pérot resonator is to incorporate nonlinear optical media with a fast response inside the interferometer. Thus, on varying the intensity of the incident beam the nonlinear phase shift changes in the nonlinear media inside the resonator. This phase addition can compensate the initial detuning of the resonator from the resonance peak leading to significant changes in the resulting transmission coefficient of the Fabry-Pérot interferometer. A detailed analysis of pulse propagation through such a device is given in the present report.

## 2. Z-scan picosecond investigations of the new organochromium CN-containing polymers.

In the second report, we described the high non-resonant electronic nonlineaity of pyrolized bis(arene) vanadium-containing polyacrylonitrile [1]. Also, as described in the first report of the previous contract (SPC 014058) we have found an extraordinarily high self-defocusing effect for non-pyrolyzed chromium-containing polyacrylonitrile (CrPAN) films cast from acetonitrile solutions [2]. During the last quarter of the present project we have continued the investigation of the cubic non-linearities on the picosecond time scale for various film-forming compositions based on bis-arenechromium complexes and CN-containing polymers. It was established previously that in the presence of air zero-valent chromium incorporated into CN- containing polymer is oxidized to the plus one oxidation state giving the Ar_2Cr^+ cation and OH$^-$ anion the latter being able to readily catalyze anionic cyclization of the cyano-groups in polymer as shown for polyacrylonitrile (Scheme 1(a)) and polyethylcyanoacrylate (Scheme 1(b)).

Scheme 1 Anionic cyclization of acrylonitrile (a) and ethylcyanoacrylate (b) units with formation of polynaphthyridine structures.

(a)
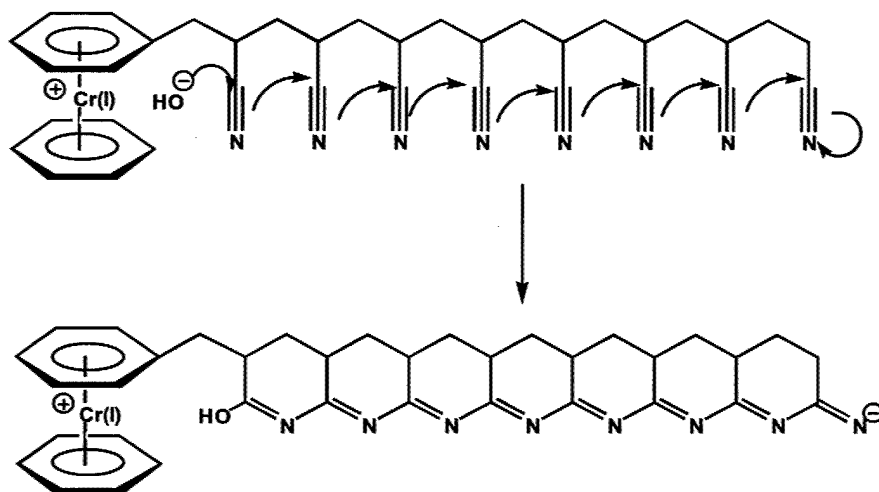
(b)
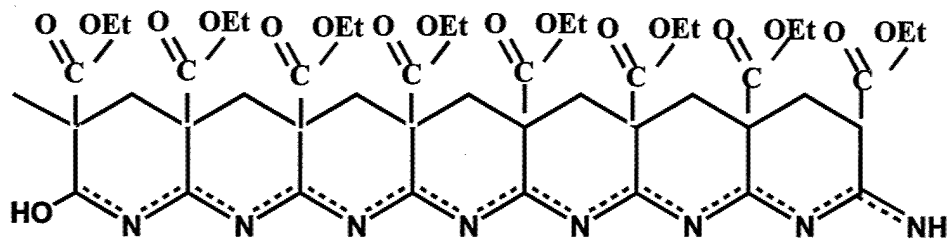
This results in the formation of long carbon-nitrogen conjugated ladder chains with a naphthyridine-type structure similar to that formed on pyrolysis of polyacrylonitrile itself [3] and consistent with the very high nonlinearity. The aim of this step of the project was to investigate the influence of the bis-(arene)metal complex concentration and the structure of its CN-containing polymeric environment on the cubic nonlinear optical properties by testing compositions of different concentration. The results of the third order non-linear optical susceptibilities measurements are presented in Table 1.

Table 1. The results of Z-scan measurement of nonlinear refractive index (n_2) and third order nonlinear optical susceptibility ($Re(\chi^{(3)})$) of the bis(arene)chromium- and CN-containing polymers.

Material*	$|n_2|$, cm^2/W	$|Re(\chi^{(3)})|$, esu	Ratio Ar$_2$Cr : PAN (PECNA)
CrPAN I	1.9×10^{-12}	9.5×10^{-11}	1 : 8
CrPAN II	3.1×10^{-14}	1.5×10^{-12}	1 : 4
CrPAN Ia (prepared one month before the measurements)	1.1×10^{-13}	5.5×10^{-12}	1 : 8
CrPECNA (bis(arene)chromium dissolved in polyethylcyanoacrilate)	3.0×10^{-14}	1.6×10^{-12}	1 : 8

*film thickness 50µm

The third-order optical nonlinearity of the films was measured by a closed-aperture Z-scan technique, which permits the characterization of the real and the imaginary parts of the nonlinear susceptibility [1]. The method has become widely used at present due to its accuracy and relative simplicity. The Z-scan experimental setup is presented in Fig. 1.
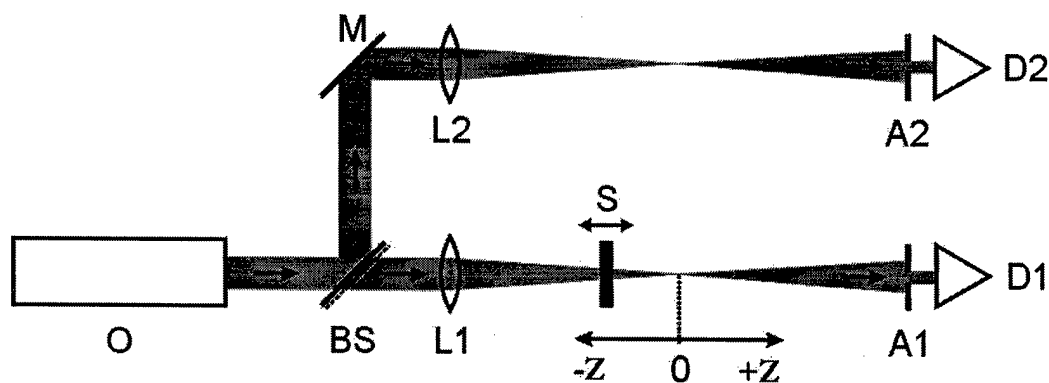

Fig. 1. Z-scan experimental setup. O – laser oscillator; BS – beamsplitter; M – mirror, L1, L2 – converging lens; S – sample; A1, A2 – aperture; D1, D2 – photodiode.

The pump radiation was the fundamental (λ = 1.054 μm) of the passively mode-locked Nd: phosphate glass laser delivering pulses with duration $\tau \approx 4$ ps and energy 100 μJ. To avoid thermal effects, the repetition rate was kept low (1 Hz). The laser was operating in the TEM_{00} mode which resulted in a Gaussian beam intensity profile. The Z-scan technique is very sensitive to the laser beam spatial intensity profile stability. To ensure compensation of its possible fluctuations an optically equal reference shoulder was included into the experimental setup. Two equal lenses L1 and L2 with 350 mm focal length focused the beam into an 85 μm diameter waist. The irradiance in the focus in the sample channel was 2.7×10^{11} W/cm^2. The diffraction length Z_0 of the focused beam was about 5 mm.

The Z-scan technique is based on the measurement of the transmittance of a nonlinear sample S through a finite aperture A1 in the far field as a function of its position Z with respect to the focal plane of converging lens L1. The refractive index of the sample can be expressed as $n = n_0 + n_2 I$ where n_0 is the linear refractive index and n_2 is the intensity-dependent refractive index proportional to the third-order nonlinear susceptibility of the sample $\chi^{(3)}$. Thus the third-order optical nonlinearity of the sample gives rise to nonlinear refraction of the laser beam, i.e. self-focusing ($n_2 > 0$) or self-defocusing ($n_2 < 0$). As a thin sample (with a thickness smaller than the diffraction length of the focused beam) is translated along the optical axis of the system in the positive direction, the beam irradiance inside the sample gradually increases before the focal plane and decreases after the plane giving rise to varying self-lensing in the sample. Monitored through the aperture by D1 photodiode this additional refraction produces characteristic transmittance curve as depicted in Fig. 2. The reference signal was detected by the D2 photodiode. A valley-peak configuration of the transmittance curve corresponds to a positive n_2 while a peak-valley configuration corresponds to a negative n_2. The difference of the peak and valley normalized transmittance values immediately gives the value for the second-order nonlinear refractive index n_2 [4].

The samples were prepared by sandwiching the polymer composition between two silica glass substrates. The thickness of the films was 50 μm which is much less than the diffraction length of the beam so the samples could be considered 'thin'. As the absorption spectra of the films show no single- or two-photon absorption at 1,054 μm, the nonlinearity of the samples was purely refractive. The n_2 values were as follows:
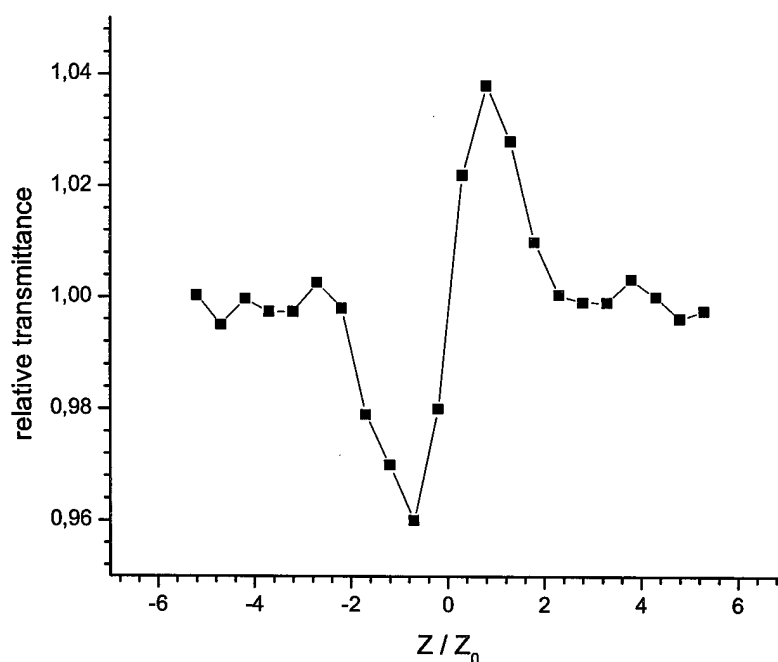
Fig. 2. Sample Z-Scan curve for CrPAN II.

Our previous investigations showed the molecule of CrPAN consists of a central $(arene)_2Cr$ species with 1-2 polyacrylonitrile arms covalently bonded to the arene ligands [5]. The data presented in Table 1 indicate that a higher concentration of the central bis-(arene) chromium species in the polymer (the ratio Ar_2Cr : PAN = 1:4) gives rise to a reduction in nonlinear optical properties (sample CrPAN II). We explain this by the decrease of the extent of π-conjugation resulting from the exceedingly short polyacrylonitrile "arms" formed at this metal complex /polymer molar ratio.

Our suggestion about the dominant rôle of the length of π-conjugation system is also confirmed by a comparison of the third-order nonlinear susceptibilities of the samples CrPAN **I** and CrPAN **Ia** . We observed a reduction in the cubic nonlinear optical properties for the sample prepared one month ago. We associate that with a slow crosslinking of the polymer taking place in the late stage of the anionic cyclization of the polyacrylonitrile units. The crosslinking causes the interruption of π-conjugation in the polynaphthyridine-type chains with formation of the following structure.

$$\cdots -H_2C-\underset{\underset{C\equiv N}{|}}{\overset{\overset{\displaystyle C=N}{\Vert}}{C}}-CH_2-\cdots$$
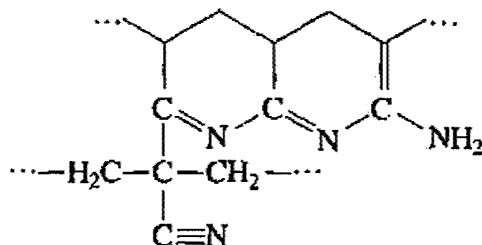
In principle, this process leading to a short life-time for the samples could be prevented by the introduction of reagents blocking the anionic centers (alcohols, for example) to the freshly prepared films.

Previously we used polyethylcyanacrylate (PECA) only as a glass-like transparent matrix for CrPAN improving the optical and mechanical properties of the CrPAN-containing films [2]. Malonodinitrile (3-5 mass.%) was used as plasticizer. The cyano-containing host polymer is quite compatible with CrPAN and can be mixed with it in all proportions giving films of excellent optical quality. Our recent investigations also revealed some new aspects of the use of another cyano-containing monomer (ethylcyanoacrylate) for non-linear optical composition preparation. We established that ethylcyanacrylate monomer, like acrylonitrile, reacted vigorously with bis-(arene)chromium(0) in the presence of strong electron acceptors giving an homogeneous polymeric film-forming product. We observed the same effect for bis-(arene)vanadium and bis-(arene)molybdenum. It is interesting to note that a test of some well-known vinyl monomers such as styrene, α-methylstyrene, methylmethacrylate and vinyl chloride did not show any reactivity of these monomers toward the transition bis-(arene)metal complexes. This indicates the important rôle played by the CN-groups in such interactions.

However, our recent investigations have revealed the principle difference between star-like macromolecules of CrPAN [5] and the structure of an analoguous product based on ethylcyanoacrylate (CrPECA). We found that the latter does not contain polymeric chains covalently bonded to the bis-arene complexes since the cyanoethylation reaction of the arene ligands does not take place in this case. The resulting product is an homogeneous solution of the (bis-arene)metal complex in polyethylcyanoacrylate. The unexpectedly high solubility of the metal complex in the polymer can be explained by supramolecular interactions between the CN-groups of the polymer and the metal atoms. Evidence for some CN- groups coordination with the central transition metal atom is confirmed by the IR spectra showing the CN absorption band shifted to lower frequencies (from 2245 cm^{-1} in pure PECA to 2190 cm^{-1} in CrPECNA). The $\chi^{(3)}$ values of the CrPECNA films (Table 1) shows the essential cubic non-linearity of that product but it is two orders of magnitude less than for the sample CrPAN **I**. This establishes the

important rôle of the star-like structure of CrPAN giving rise to more extensive conjugation and also metal – polymer charge transfer known to result in high electronic cubic non-linearities. Nevertheless, Cr-contaning PECNA is a very promising component improving the optical and mechanical properties of the nonlinear optical films based on CrPAN.

3. A new method of two beam coupling with spectral resolving; application in a cubic optical nonlinearity study of bis(arene)chromium-containing polyacrylonitrile in the femtosecond range of pulse duration.

Method description [6, 7]:

Two-beam coupling with spectral resolving is a new sensitive method for the determination of nonlinear optical coefficients in various media. There exist equations that describe the propagation of strong pump pulse and weak probe pulse at the same time in a nonlinear optical medium. We take into account cross-phase modulation, self-phase modulation for the strong beam, linear and two-photon absorption for the theoretical analysis.

$$
\begin{cases}
\dfrac{\partial I_{pu}}{\partial z} + \dfrac{1}{u}\dfrac{\partial I_{pu}}{\partial t} = -(\alpha + \beta I_{pu}) \cdot I_{pu}, \\[2mm]
\dfrac{\partial \phi_{pu}}{\partial z} + \dfrac{1}{u}\dfrac{\partial \phi_{pu}}{\partial t} = k\gamma I_{pu}, \\[2mm]
\dfrac{\partial I_{p}}{\partial z} + \dfrac{1}{u}\dfrac{\partial I_{p}}{\partial t} = -(\alpha + 2\beta I_{pu}) \cdot I_{p}, \\[2mm]
\dfrac{\partial \phi_{p}}{\partial z} + \dfrac{1}{u}\dfrac{\partial \phi_{p}}{\partial t} = 2k\gamma I_{pu}.
\end{cases}
$$

α – linear absorption coefficient, β – coefficient of two-photon, $\beta \sim Im\chi^{(3)}$, $\gamma = 4\pi n_2/cn$ – coefficient, proportional nonlinear refractive index n_2 and real part of third-order nonlinear optical susceptibility $Re\chi^{(3)}$, $n_2(cm^2/Wt) \approx 1/50 \cdot Re\,\chi^{(3)}(in\ esu)$.

It is required that the nonlinear phase shifts $\Delta\Phi = k\gamma I_{pu}L$, $q = \beta I_{pu}L$ should be less than 0.1 for good theoretical approximation.

For Gaussian pulse shape $E = E_0 exp(-t^2/t_0^2)$ the following result for relative changes of the spectral component follows from the above equations.

$$
\frac{\Delta T}{T}(\tau, \delta\omega) = \frac{2}{\sqrt{3}}\exp(\delta\omega^2 t_0^2/6)\exp(-2\tau^2/3t_0^2)(2\Delta\Phi\sin(2\tau \cdot \delta\omega) - q\cos(2\delta\omega \cdot \tau/3)).
$$

For a "signal-to-noise" ratio of at least about 150 registered for our equipment the nonlinear phase shift is equal to:

$$\Delta\Phi = 0.0004.$$

An alternative method for nonlinearity detection is two-beam coupling with autocorrelation function analysis.

Before the experimental studies we made some attempts to find similar methods with the same sensitivity. One of the most successful variants was the following. We calculated the autocorrelation function for the probe beam, using the approximation mentioned in the main method:

$$FE(\tau, t_K) = E_0^2 t_0 \sqrt{\frac{\pi}{2}} \cdot (2\cos(\omega t_K)\exp(-t_K^2 / 2t_0^2) + 2\Delta\Phi\sin(\omega t_K)(\exp(2t_K^2 / t_0^2) - 1)\exp(-t_K^2 / 2t_0^2 - 2\tau_K / t_0^2))$$

The largest changes in autocorrelation function were at root points of the autocorrelation function in the case of zero nonlinearity ($\Delta\Phi=0$). With the same estimated level of "signal-to-noise" ratio of a minimum of about 150 the nonlinear phase shift is equal to $\Delta\Phi = 0.003$. So this method is about ten times less sensitive than the previous one.
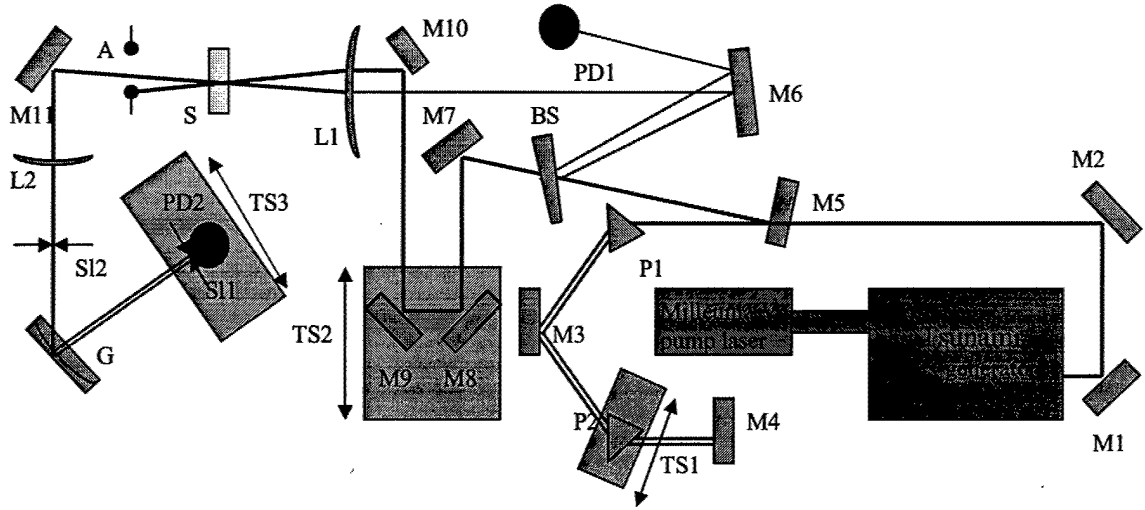
Setup description:

Experimental setup: M- high-reflective mirror, P- prism, TS- translator stage, BS- beam splitter, PD- photodiode, L- lens, S- investigated sample, A- aperture for beam selection, Sl- slit, G- grating.

Millennia V pump laser pumps Tsunami fs-generator. Tsunami generates 35-fs pulses with average power of 100-250 mW at repetition rate 80 MHz. Central wavelength of laser radiation is 795-800 nm.

The dispersion compensator consists of prisms P1 and P2 on translation stage TS1, mirrors M3, M4. Its adjustment allows to compensate dispersion in the optical elements before the polymer film to provide minimal pulse duration in the polymer sample. There is a small vertical detuning

of the beams in the compensator for changing the direction of walking of the backward beam after the compensator with mirror M5. The beam from M2 to P1 is higher than M5.

The thin beamsplitter BS separates the initial beam into 3 parts; the strongest one passes through the beamsplitter and goes to part of delay changing, the two weak pulses being used as testing or probe pulse in the sample and for real-time laser power control.

Part of delay changing allows the change in delay of the pump pulse in the sample. Its translation stage TS2 (with two mirrors M8 and M9) can be positioned with an accuracy of 7 nm for sufficient experimental points.

After reflections from mirrors M6 and M10 the probe and pump beams are focused with lens L1 in the sample S. The focal length is 0.14 m, so we can get the intensity of the pump beam in the sample in the range of 1-3 GW/cm^2. To obtain the autocorrelation function for the testing beam we used a LiIO$_3$ crystal for producing the second harmonic.

A Rowland spectrometer was used for the probe pulse spectral analysis. The lens L2 focuses the beam on the entrance slit and increases the sensitivity of the signal received by photodetector PD2.
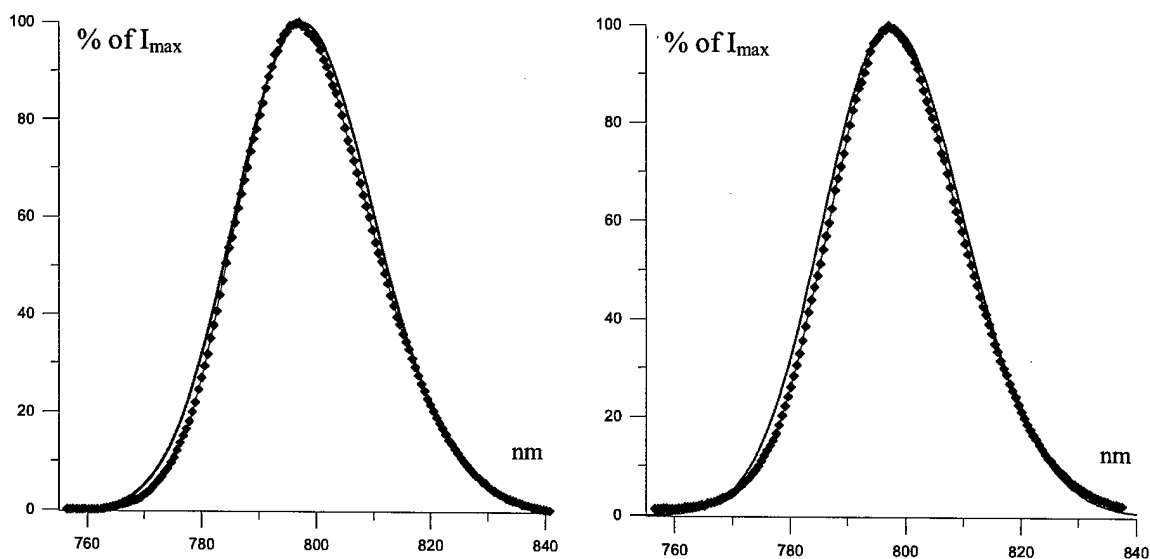
Initial spectrum of laser radiation with Gaussian fit therefore the spectral bandwidth of the laser pulse is 20-26 nm at half-maximum level.
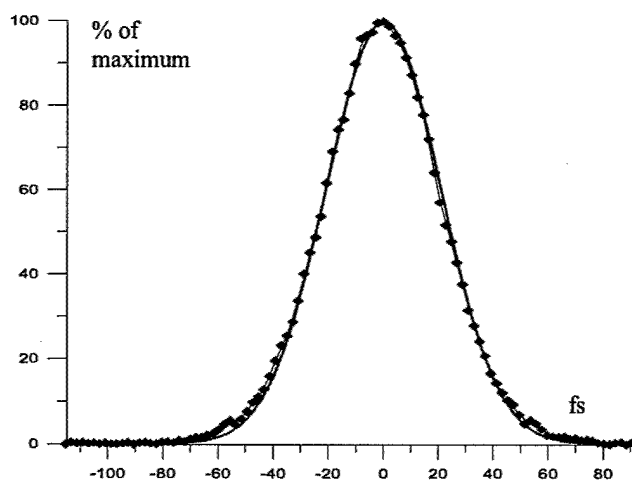
Autocorrelation function:

The autocorrelation function and envelope for the theoretical curve, corresponding to 42 femtosecond pulse duration. The small peaks at the bottom of this dependence are the result of incomplete compensation of the pulse dispersion.

There is a good correspondence between the spectral and autocorrelative diagnostics of the pulse parameters.
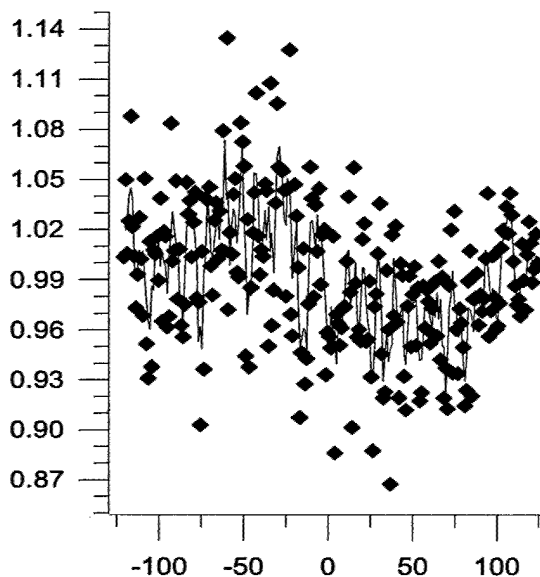
Results of measurements for polymer samples

CrPAN Ia:

We average many scans in order to detect the nonlinearity and decrease the noise of various types.

The following is a typical scan for polymer sample dependence of the normalized (on spectral component without pump, or far from zero delay) spectral component of the probe pulse on the pump-to-probe delay. The line corresponds to the averaging of three scans. The spectral detuning is 21 nm (or approximately 2σ in half-width at half-maximum units).

The calculated theoretical fit for this data gives the nonlinear refractive index for the studied samples of about $-2\text{-}3\cdot10^{-14}$ cm^2/W with about 100% relative error (because of the huge noise level).
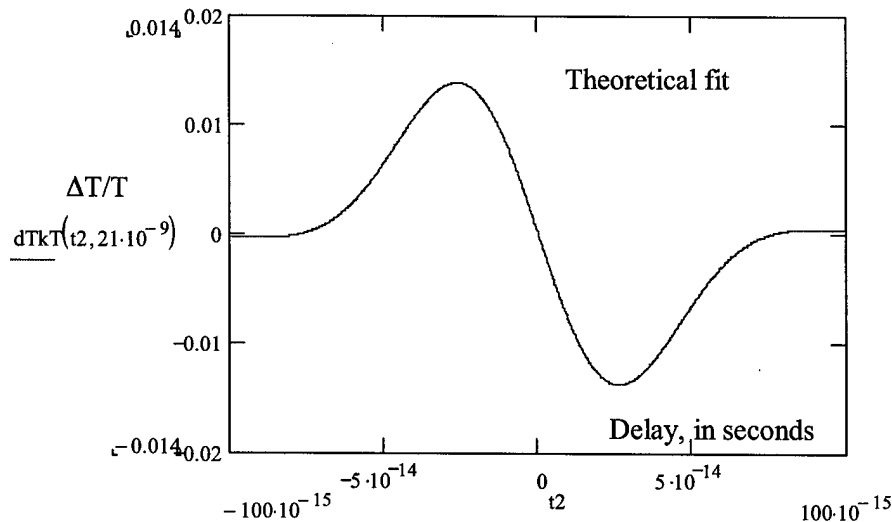
4. Theoretical calculation of all-optical switching in a Fabry-Pérot resonator containing a nonlinear polymer layer.

Introduction:

The main idea of fast optical switching in a nonlinear Fabry-Pérot resonator is the incorporation of nonlinear optical media with fast response inside the interferometer. Thus, by varying the intensity of the incident beam the nonlinear phase shift changes in the nonlinear media inside the resonator. This phase addition can compensate the initial detuning of the resonator from the resonance peak leading to a significant change in the resulting transmission coefficient of the Fabry-Pérot interferometer. A detailed analysis of pulse propagation through such a device is presented in this report.

Linear Fabry-Pérot interferometer:

The phase addition between two consequent reflections in the resonator is given by:

$$2\phi = 2kL\cos\theta = \frac{4\pi n_r \nu}{c} L\cos\theta; \quad \phi = 2\pi L'\nu/c; \quad L' = n_r L\cos\theta.$$

The amplitude of the electric field in the output beam is:

$$E_t = \sum_{l=1}^{\infty} E_l = (E_0 t_1 t_2 e^{i\phi'})\sum_{m=0}^{\infty} (r_1 r_2)^m \exp(2mi\phi) = \frac{E_0 t_1 t_2 e^{i\phi'}}{1 - r_1 r_2 \exp(2i\phi)}.$$

The transmission coefficient on intensity for the interferometer is:

$$T = \frac{|E_t|^2}{|E_0|^2} = \frac{t_1^2 t_2^2}{1 - 2r_1 r_2 \cos 2\phi + r_1^2 r_2^2}.$$

Alternatively, the same equation for transmission using reflection coefficients on intensity for mirrors (mirrors are without losses) $T = t^2$, $R = r^2$, $T + R = 1$:

$$T = \frac{(1 - R_1)(1 - R_2)}{(1 - \sqrt{R_1 R_2})^2 + 4\sqrt{R_1 R_2}\sin^2\phi}.$$

The sharpness of the interferometer is:

$$F = \Delta\nu_{fsr}/\Delta\nu_c = \frac{\pi \cdot \sqrt[4]{R_1 R_2}}{1 - \sqrt{R_1 R_2}}.$$

Fabry-Pérot interferometer with nonlinear layer inside, without absorption.

The refraction coefficient for the nonlinear sample is:

$$n_r = n_0 + n_2 I.$$

Initially, the resonator is not at the resonance point and has initial phase detuning. By increasing the intensity we can change the refractive index of the media, so the effective length of the resonator (or optical length) changes. The optical length is responsible for the resonant properties of the interferometer, i.e. what resonance point changes. When the initial phase detuning has the same value as the nonlinear phase addition $\Phi_{nl} = k n_2 I l$, but opposite sign, we will get resonance transmission. In other words, we get optical switching

Estimation for suitable pulse duration.

Three values, characterizing the nonlinear Fabry-Pérot interferometer (in decreasing order, the next figure should be much smaller):

A). Frequency detuning, equal to nonlinear phase addition in nonlinear optical media.

B). Spectral bandwidth of interferometer transmission. It is less than the spectral interval between two consequent modes of the interferometer (see sharpness above). For 100 micron interferometer base and 1064 nm wavelength the spectral interval is equal to $2 \cdot 10^{13}$ s^{-1}.

C). Pulse spectral bandwidth. For 40 ps pulses: $\Delta\omega = 1{,}1 \cdot 10^{10}$ s^{-1}. (For femtosecond pulses it is impossible to get interference inside such an interferometer, because even a 100 fs pulse has a length $3 \cdot 10^{-5}$ m or 30 micron).

Switching possibility estimation using the investigated polymers.

Nonlinear refraction indexes for studied polymers: -10^{-12} cm^2/W.

Linear absorption for investigated polymers: 5-20 cm^{-1}

Picosecond pulses characteristics:

10-50 µJ, 40 ps, 1064 nm, focused in circle with diameter 0.1 mm.

Nonlinear phase addition for the Fabry-Pérot interferometer with polymer layer: $\Phi \sim 1$.

Nonlinear Fabry-Pérot interferometer containing a polymer layer with provision for linear absorption.

Polymer film

Front mirror

Rear mirror
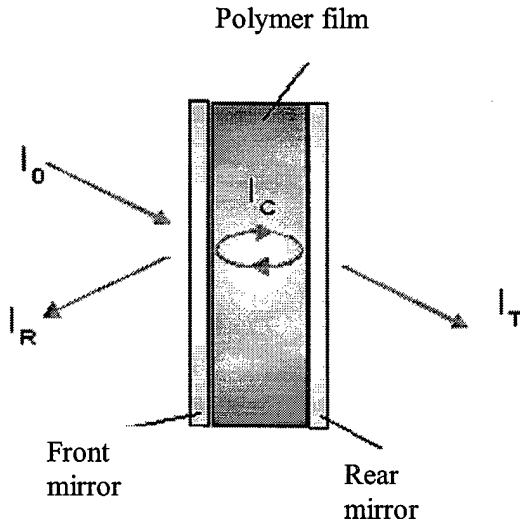
Relations between intensities of the incident beam I_0, the beam inside the interferometer I_c, the reflected beam I_r and the transmitted beam I_t:

$$\theta = \frac{2\pi d n_2 I_c}{\lambda} + \delta -$$ phase detuning in interferometer with initial phase detuning δ.

$$n_2 = \frac{4\pi^2 \, \mathrm{Re}[\chi^{(3)}]}{c n_0}$$

$$I_t = \frac{\alpha d (1 - R_B) \exp(-\alpha d)}{(1 - \exp(-\alpha d))(1 + R_B \exp(-\alpha d))} I_c,$$

$$I_r = \frac{\alpha d (1 - R_B \exp(-2\alpha d))}{(1 - \exp(-\alpha d))(1 + R_B \exp(-\alpha d))} I_c,$$

$$I_c = \frac{(1 - R_F)(1 - \exp(-\alpha d))(1 + R_B \exp(-\alpha d))}{\alpha d [(1 - \sqrt{R_F R_B} \exp(-\alpha d))^2 + 4\alpha d \sqrt{R_F R_B} \exp(-\alpha d) \sin^2 \theta]} I_0,$$

$$I_t \left(1 + \frac{4\sqrt{R_F R_B} \exp(-\alpha d)}{[1 - \sqrt{R_F R_B} \exp(-\alpha d)]^2} \cdot \sin^2 \left(\frac{2\pi n_2 (\exp(\alpha d) - 1)(1 + R_B \exp(-\alpha d))}{\lambda \alpha (1 - R_B)} I_t + \delta \right) \right) -$$

$$-\frac{(1-R_B)(1-R_F)\exp(-\alpha d)}{(1-\sqrt{R_F R_B}\exp(-\alpha d))^2}I_0=0,$$

$$(I_0-I_r)\cdot\left(1+\frac{4\sqrt{R_F R_B}\exp(-\alpha d)}{[1-\sqrt{R_F R_B}\exp(-\alpha d)]^2}\cdot\sin^2(\frac{2\pi n_2(\exp(\alpha d)-1)(1+R_B\exp(-\alpha d))}{\lambda\alpha(1-R_B)}(I_0-I_r)+\delta)\right)-$$

$$-\frac{(1-R_B)(1-R_F)\exp(-\alpha d)}{(1-\sqrt{R_F R_B}\exp(-\alpha d))^2}I_0=0.$$

The above equations were used for the calculation of the dependencies of the pulse energy transmission through the Fabry-Pérot resonator.

On the following graph the typical dependence of the Fabry-Pérot resonator transmission on the wavelength of the laser radiation is shown. Each curve corresponds to various peak intensities of the beam.
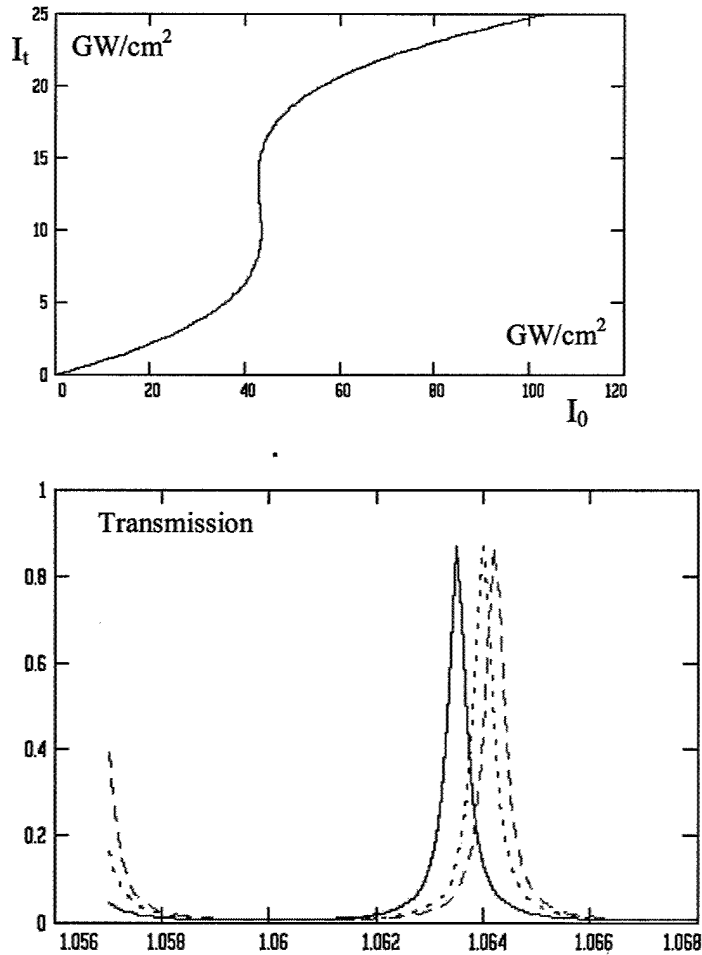
The final dependence of the transmitted laser pulse energy on the incident laser pulse energy demonstrates the possibility of optical switching with the present polymer samples.
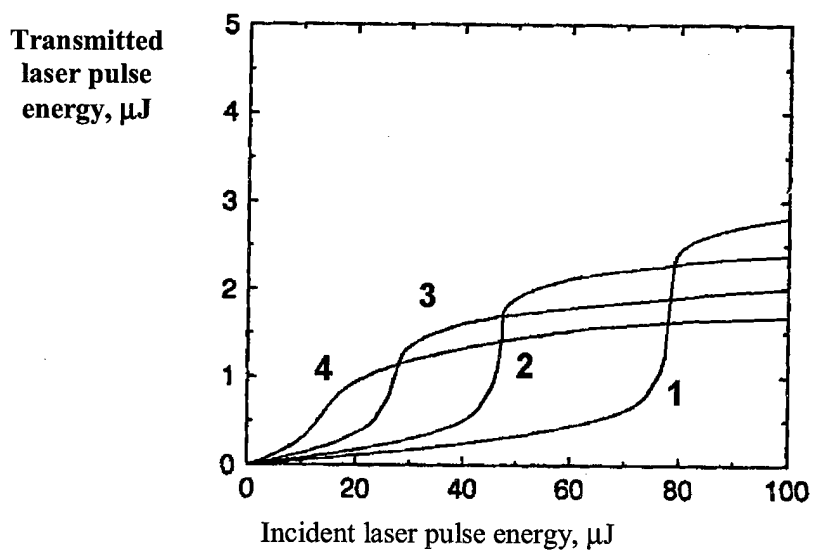
(For various curves peak intensities are I=5, 10, 20, 30 GW/cm^2)

5. Conclusions

Large third order nonlinear optical susceptibility coefficients with femtosecond time of initialization were found for new chromium-contained organometallic polymers. Investigations using a femtosecond laser and new sensitive method of spectrally resolved two-beam coupling have confirmed studies in the picosecond range. The main results of the latter picosecond studies was the demonstration of large electronic optical nonlinearities in the samples studied. Further improvement in the experimental setup will allow us to detect two-photon absorption in the polymers and to decrease the experimental error for the nonlinear refractive index and the real part of the third order optical susceptibility.

The possibility of fast optical switching by using nonlinear a Fabry-Pérot interferometer containing a nonlinear polymer layer has been established. A strong dependence of the nonlinear resonator propagation coefficient on peak intensity (or pulse energy at fixed duration) is found for certain parameters of this device, such as reflection coefficients of front and back mirrors, layer width and the nonlinear refractive index of polymer. The problem of creating optical switchers with initial requirements lies in the precise control of layer thickness inside the interferometer and the formation of an homogeneous polymer layer with high electronic third order nonlinearity.

6. Declaration

1)   In accordance with the Defense Federal Acquisition Regulation 252.227-7036, Declaration of Technical Data Conformity (Jan 1997), the Contractor, Université Montpellier II, hereby declares that, to the best of its knowledge and belief, the technical data delivered herewith under contract No. FA8655-02-M4074, is complete, accurate and complies with all requirements of the contract.

2)   In accordance with the requirements in Federal Acquisition Regulation 52.227-13, Patent Rights - Acquisitions by the U.S. Government (Jun 1989), the contractor certifies that there were no subject inventions to declare as defined in FAR 52.227-13, during the performance of contract No. FA8655-02-M4074.

7. References

[1]   L. G. Klapshina, V. V. Semenov, Z. Y. Fominykh, G. A. Domrachev, W. E. Douglas, O. L. Antipov, and A. S. Kuzhelev, "Novel vanadium-containing polymers prepared from bis(arene)vanadium and acrylonitrile: third-order non-linear optical properties," *Polymer International*, vol. 51, pp. 1178-1183, 2002.

[2]   A. V. Afanas'ev, A. P. Zinoviev, O. L. Antipov, B. A. Bushuk, S. B. Bushuk, A. N. Rubinov, J. Y. Fominih, L. G. Klapshina, G. A. Domrachev, and W. E. Douglas, "Picosecond z-scan measurements of nonlinear optical susceptibility of films and solutions of novel organometallic polymers," *Optics Communications*, vol. 201, pp. 207-215, 2002.

[3]   J. Pospisil, M. Samoc, and J. Zieba, "Third-order nonlinear optical properties of a ladder polymer obtained by pyrolysis of polyacrylonitrile," *European Polymer Journal*, vol. 34, pp. 899-904, 1998.

[4]   M. Sheik-Bahae, A. A. Said, T.-H. Wei, D. J. Hagan, and E. W. van Stryland, "Sensitive measurements of optical nonlinearities using a single beam," *IEEE J. of Quantum Electronics*, vol. 26, pp. 760-769, 1990.

[5]   G. A. Domrachev, W. E. Douglas, B. Henner, L. G. Klapshina, V. V. Semenov, and A. A. Sorokin, "Bis(arene) chromium-containing polyacrylonitrile and its thermolysis products: Synthesis, characterization and magnetic properties," *Polymers for Advanced Technologies*, vol. 10, pp. 215-222, 1999.

[6]   P. S. Spencer and K. A. Shore, "Pump-probe propagation in a passive Kerr nonlinear optical medium," in *Journal of the Optical Society of America B: Optical Physics*, vol. 12, 1995, pp. 67-71.

[7]   I. Kang, T. Krauss, and F. Wise, "Sensitive measurement of nonlinear refraction and two-photon absorption by spectrally resolved two-beam coupling," *Optics Letters*, vol. 22, pp. 1077-1079, 1997.